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| 14. ABSTRACT Improvements in thermal and physical properties of epoxy resin systems have been demonstrated in the past through the influence of fillers. However, these improvements often come with a significant cost to processability. This paper examines the influence of nanofillers on a multifunctional epoxy resin system in terms of processability and thermal properties. The nanocomposites explored included nanosilica, linear calcium silicate (wollastonite), and polyhedral oligomeric silsesquioxane (POSS) in CYCOM® 977-3 resin. Composites with three to five weight percent of nanofillers were produced using IKA high shear mixers. The thermal and flow properties of the composites were evaluated using Dynamic Mechanical Thermal Analysis (DMTA) and parallel plate rheology. The microstructure of the composite was explored using Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Each of the nanofillers used in this study showed a small improvement in T _g over the neat epoxy. However, the addition of nanosilica dramatically increased the viscosity of the neat resin in contrast to the addition of wollastonite or POSS. The wollastonite showed no degradation in clarity and did not significantly increase the viscosity of the resin. | | | | | |
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PROCESSING OF MULTIFUNCTIONAL EPOXY RESINS MODIFIED WITH SILICON BASED NANOMATERIALS

Amy R. Spero^{1*}, Darrell Marchant¹, Lisa Viculis², and Joseph M. Mabry¹

¹Air Force Research Laboratory, Propulsion Materials Application Branch, AFRL/PRSM, 10
Saturn Blvd, Bldg. 8451, Edwards AFB, CA 93524

²Cytec Engineered Materials, 1440 N. Kraemer Blvd., Anaheim, CA 92806

*Corresponding author: amy.spero@edwards.af.mil

ABSTRACT

Improvements in thermal and physical properties of epoxy resin systems have been demonstrated in the past through the influence of fillers. However, these improvements often come with a significant cost to processability. This paper examines the influence of nanofillers on a multifunctional epoxy resin system in terms of processability and thermal properties. The nanocomposites explored included nanosilica, linear calcium silicate (wollastonite), and polyhedral oligomeric silsesquioxane (POSS) in CYCOM® 977-3 resin. Composites with three to five weight percent of nanofillers were produced using IKA high shear mixers. The thermal and flow properties of the composites were evaluated using Dynamic Mechanical Thermal Analysis (DMTA) and parallel plate rheology. The microstructure of the composite was explored using Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Each of the nanofillers used in this study showed a small improvement in T_g over the neat epoxy. However, the addition of nanosilica dramatically increased the viscosity of the neat resin in contrast to the addition of wollastonite or POSS. The wollastonite showed no degradation in clarity and did not significantly increase the viscosity of the resin.

KEYWORDS: Nanomaterials/Nanocomposites/Nanotechnology, Cure/Process – Evaluation, Resin/Materials – epoxy

1. INTRODUCTION

Epoxy resins are used for many high performance applications due to their exceptional properties. They are typically low density materials with excellent electrical, thermal, mechanical and chemical properties. Epoxy parts are rigid and have good dimensional stability over a wide temperature range. Due to the wide variety of epoxies and epoxy reinforced materials, it is possible to tailor them to almost any application. Epoxy resins are routinely used as coatings due to their chemical resistance, impact and abrasion resistance, and their capability as adhesives. Their electrical and mechanical capabilities also make epoxies ideal for use in electrostructural applications. They are especially suitable for composites due to good fiber adhesion in fiber reinforced materials [1].

The resin selected for this study is CYCOM® resin 977-3 because it is a high performance ($T_g > 200$ °C) co-continuous toughened epoxy resin used in a myriad of applications. It is typically used in aircraft and other applications where impact resistance and high temperature performance are critical. This resin is primarily used as a matrix in fiber reinforced polymer matrix

composites and can be processed in both RTM and autoclave processes as well as press molding [2].

Epoxies are reinforced with continuous fibers such as glass, carbon and aramid fibers and fillers like graphite, asbestos and clays. While the incorporation of fillers allows the mechanical and thermal properties to be tailored, the ease of processability often suffers as a result. These processing difficulties can be mitigated by using low volume fractions of nanofillers. In contrast to talc, mica, silica, and carbon black which require >30 wt% incorporation to yield significant improvement in physical properties, nanofillers yield similar enhancements with less than 4 vol % incorporation [3].

However, the incorporation of nanofillers is not without effect on viscosity at high loadings. Koo et al. found that when particle loadings are small (around 1%) and the resin viscosity is low, there is little or no benefit in mechanical properties. In order to increase the mechanical properties, higher particle loadings are necessary. These loadings often result in excessive viscosity and non-uniform fiber “wet-out” during impregnation of fibers or fabric [1]. This effect may be mitigated by the use of solvents. Brown found that the addition of low boiling point solvents such as acetone to enhance mixability and processability of organically modified layered silicate/epoxy mixtures does not alter the structure or properties of the final nanocomposite [3]. Therefore, solvent variation was one of the methods examined in this study to mitigate the processing difficulties of the nanofilled epoxy resin system.

The purpose of this paper is to analyze and understand the effect of various mixing procedures on the T_g of several epoxy-nanocomposite blends. The authors used the T_g of nanofilled CYCOM® 977-3 epoxy as a gauge of processing success and examined the viscosity and dispersion of the nanocomposites.

2. EXPERIMENTAL

2.1 Materials The Cytec Engineered Materials composition 977-3 (CYCOM® 977-3), which was used in this study, is a four component, multifunctional epoxy system. These components are referred to as components A, B, C and D in this paper. Three types of nanoparticles were used, a nanosilica, a linear calcium silicate, and a polyhedral oligomeric silsesquioxane (POSS).

The nanosilica used was Degussa Corporation Aerosil® R202, a fumed silica with a polydimethylsiloxane surface treatment and a mean particle size of 14 nm. Its applications include use in adhesives or sealants and use as a thickening agent or anti-settling agent in epoxy, polyurethane or vinylester resins. It can be described as highly flocculent and has a very low tap density of 0.06 g/cc and a specific surface area of 100 ± 20 m²/g [4].

The linear calcium silicate used in the study was Fibertec Inc. Wollastonite 520H, an acicular particle with a hydrophobic surface treatment. It has a typical aspect ratio of 20 and an average bundle diameter of 5 microns. Its tapped density is 0.59 g/cc and surface area is 2.0 m²/g [5].

DodecaPhenyl-POSS or Ph₁₂T₁₂ shown in Figure 1 was the type of POSS used. POSS is a three dimensional precise nanoparticle with a rigid, inorganic core and an organic functionality, in this

case phenyl. Due to their physical size, the incorporation of POSS into polymers typically serves to reduce chain mobility, often improving both thermal and mechanical properties. $\text{Ph}_{12}\text{T}_{12}$ has an agglomerated particle size distribution of 5-100 μm with an individual particle size of less than 3 nm and a specific surface area of approximately 0.50 m^2/g .

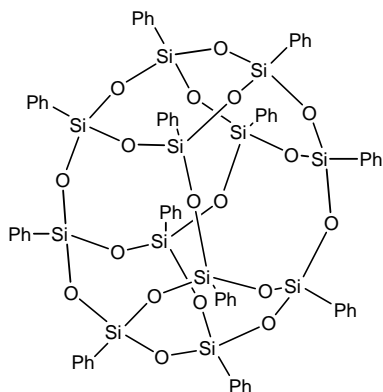


Figure 1. DodecaPhenyl-POSS ($\text{Ph}_{12}\text{T}_{12}$) structure

2.2 Sample Preparation The nanofillers were manually mixed into components A and B of the 977-3 epoxy system in order to wet the particles. The mixtures were then subjected to high shear mixing using an IKA Labor Pilot DR high shear mixer shown in Figure 2. This mixer uses a rotor stator design with three mixing stages, Figure 2b. The material is introduced into the top of the mixer and is accelerated to the edge of the first stage by centrifugal force. The material exits each stage through channels in the stator which get progressively smaller with each stage. When the material reaches the bottom the third stage drives the material out of the mixer. This procedure was repeated ten times to ensure thorough mixing. Finally, components C and D of the epoxy system were mixed in using one of two mixing techniques and the samples were cured.

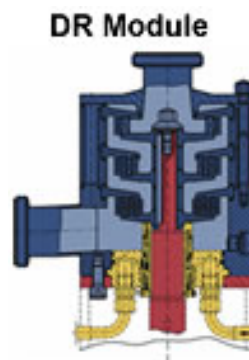


Figure 2. a) Photograph of the IKA Labor Pilot 2000/4 high shear mixer. b) Cartoon of the inside of the DR segmented module [6].

The first procedure that was investigated to mix components C and D into the epoxy system was using a stir bar in the mixture while heating the materials in an oil bath at 70 °C. To aid in this mixing process, the authors felt that a solvent should be used to ease the mixing process due to the viscosity of the materials. Two different solvents were used, acetone and methylene chloride, to reduce the viscosity. This process variation and its effect are further discussed in section 3.3. Component C was added and mixed for a duration of one hour and then component D was mixed in for an additional 5 minutes. The material was poured out onto non-stick paper and degassed for one hour at 75 °C.

The second procedure used to incorporate the C and D components into the epoxy system was by using an IKA T25 Labortechnik rotor-stator mini high shear mixer shown in Figure 3. This device uses shear to mix the materials and is better suited for small batches than the IKA Labor Pilot. Due to the efficiency of the mixer, no solvents were used and two different mix times were investigated. Component C was mixed into the material for 5 or 30 minutes and component D was added and mixed for an additional 5 minutes. The material was poured out onto non-stick paper and degassed for one hour at 75 °C.



Figure 3. IKA T25 Labortechnik Rotor Stator mini high shear mixer

After degassing, the material formed a flat plaque which could be peeled off of the paper. This plaque was cut into strips and placed into an aluminum mold previously baked with Loctite Frekote mold release. The mold contained 12 DMTA cutouts to produce final sample dimensions of approximately 7.8 mm wide by 1.2 mm thick by 25 mm long. The samples in the mold were rolled flat and cured using the procedure described below [7] and illustrated in Figure 4.

Heat samples to 140 °C over 2 hours (0.8 °C/min)
Hold at 140 °C for 2 hours
Heat samples to 180 °C over 2 hours (0.3 °C/min)
Hold at 180 °C for 6 hours
Cool slowly (~6 hours)

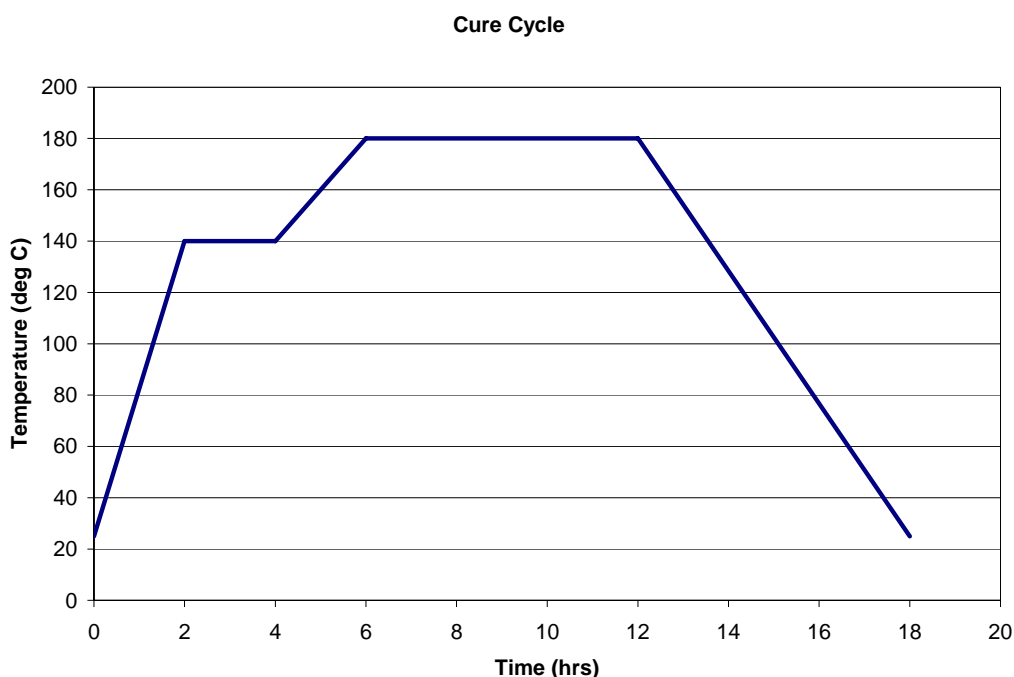


Figure 4. Cure cycle of 977-3 epoxy nanocomposites

2.3 Sample analysis The authors investigated the thermal properties of the material, the processability and the dispersion of the particles within the material. The thermal properties were parameterized by the glass transition temperature and the processability was measured by viscosity. The dispersion was measured using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and optical clarity.

The glass transition temperatures of the fully cured materials were measured using a Rheometric Scientific Dynamic Mechanical Thermal Analyzer (DMTA) model DMTA 5. Samples were tested in three point bend mode and tests were run at 5 °C/min up to 300 °C, 1% Strain, 1Hz frequency.

Viscosity was measured using parallel plate rheology on the epoxy resin system before the curing agent was added. Parallel plate steady state rotational tests were performed on a Paar Physica MCR 500 at shear rates ranging from 10^{-3} to 10^2 s $^{-1}$. Samples were tested at room temperature and at 80 °C.

The Transmission Electron Microscope (TEM) used was a JOEL JEM 2010 at an accelerating voltage of 200 keV. The samples for TEM were cut with an Ultramicrotome at room temperature with a diamond knife. The Scanning electron microscopy (SEM) analysis was performed on samples polished using diamond lapping film. The images were taken using an ISI CL6 operating at 15 keV equipped with a Kevex X-ray detector. Elemental mapping was performed using energy dissipation X-ray analysis (EDAX) with IXRF Systems analysis software.

3. RESULTS AND DISCUSSION

3.1 Nanoparticle Dispersion TEM images were taken of 3% R202 samples to determine if the particles were well dispersed. The images in Figure 5 show that particles are dispersed after 30 minutes of mixing with the IKA T25 high shear mixer. The particles primarily exist as aggregates about 100 nm in diameter and are evenly dispersed. Images in Figure 6 taken of the material at elevated mixing temperature, 70 °C, show an even higher level of dispersion achieved. This is illustrated by the reduction in the number of aggregates.

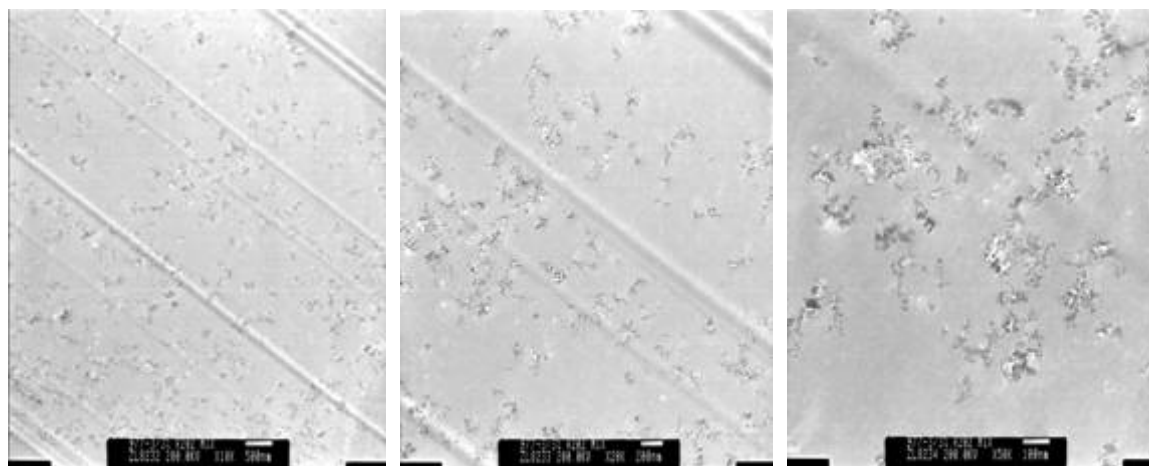


Figure 5. TEM images of 3 wt% R202 mixed for 30 minutes at ambient temperature where the scale bar is 500 nm (left), 200 nm (middle) and 100 nm (right).

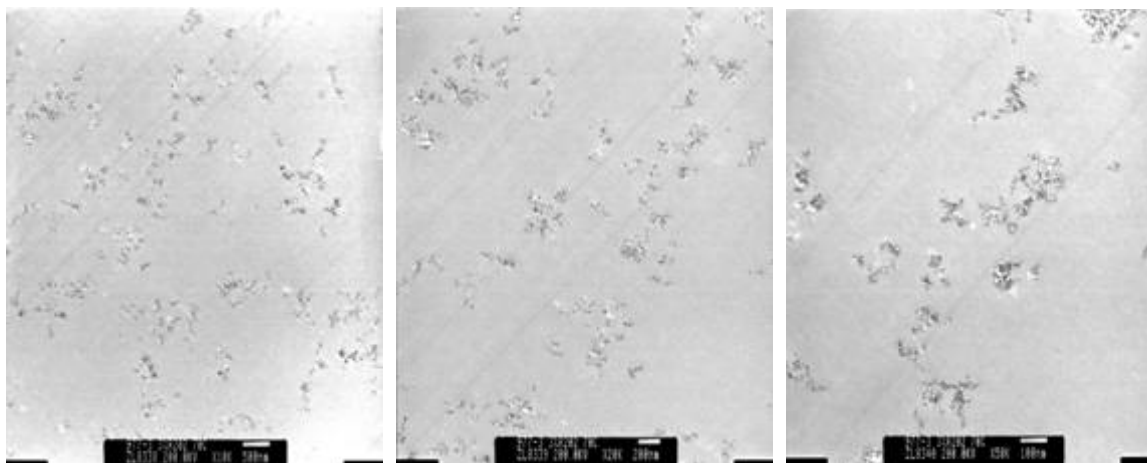


Figure 6. TEM images of 3 wt% R202 mixed for 30 minutes at 70 °C where the scale bar is 500 nm (left), 200 nm (middle) and 100 nm (right).

TEM images were also taken of 5 wt % 520H wollastonite and 5 wt% $\text{Ph}_{12}\text{T}_{12}$ to determine the difference in dispersion between the various nanofillers. Both materials exhibit only a small number of large aggregates in the TEM images, Figures 7 and 8. This may imply that the majority of the filler is dispersed. Since TEM only views a very small portion of the sample, roughly 7 μm by 9 μm , the dispersion was further investigated for the 5 wt% 520H sample using SEM for imaging, Figure 9, and elemental analysis, Figure 10. Elemental mapping of calcium and silicon, found only in the nanofiller, shows that despite the large aggregates, the particles are uniformly dispersed. The majority of the particles are so small that they can only be seen by improving the brightness and contrast of the images.

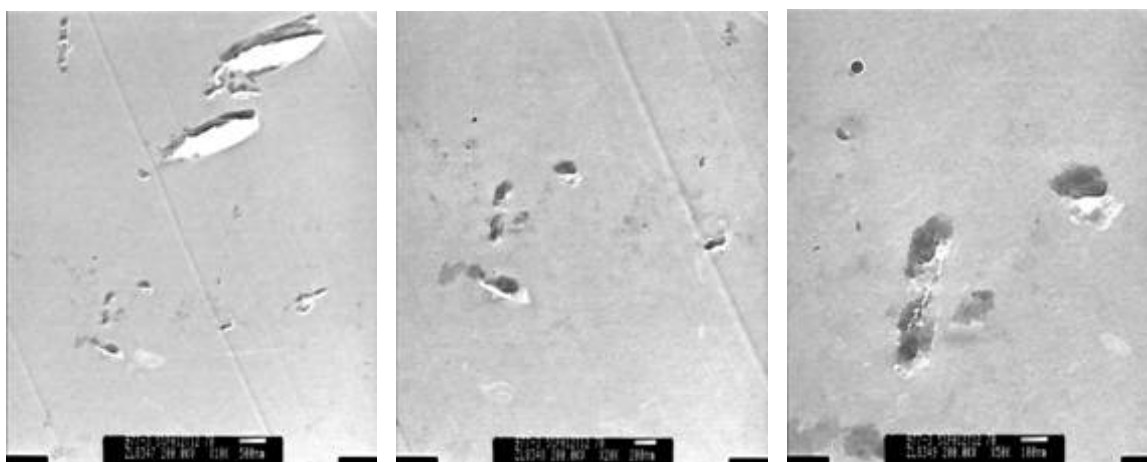


Figure 7. TEM images of 5 wt% $\text{Ph}_{12}\text{T}_{12}$ mixed for 30 minutes at 70 °C where the scale bar is 500 nm (left), 200 nm (middle) and 100 nm (right).

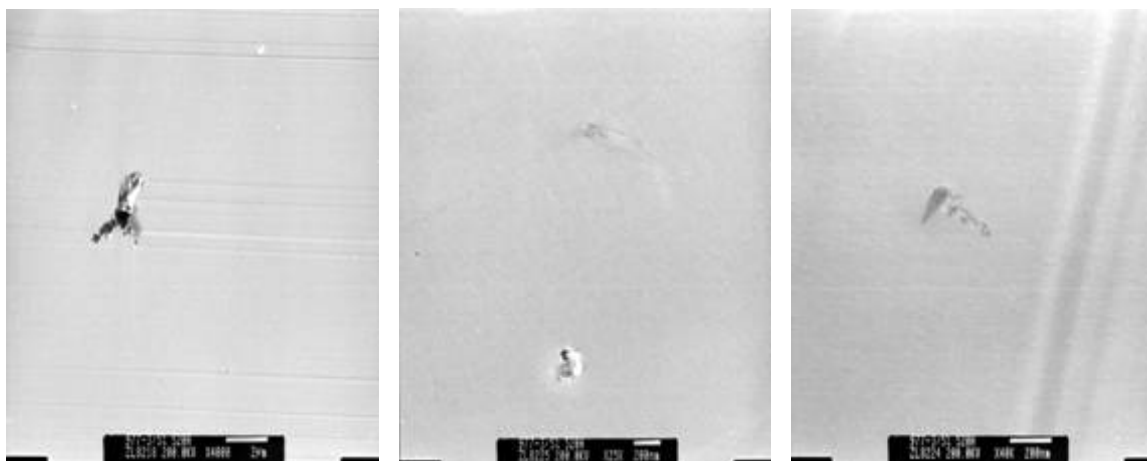


Figure 8. TEM images of 5 wt% 520H Wollastonite mixed at ambient temperature for 5 minutes where the scale bar is 2 μm (left) and 200 nm (middle and right).

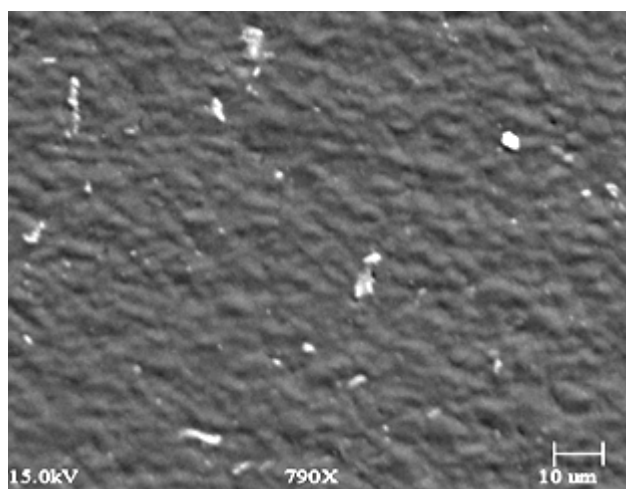


Figure 9. SEM image of 5 wt% 520H Wollastonite mixed at 70 °C for 30 minutes

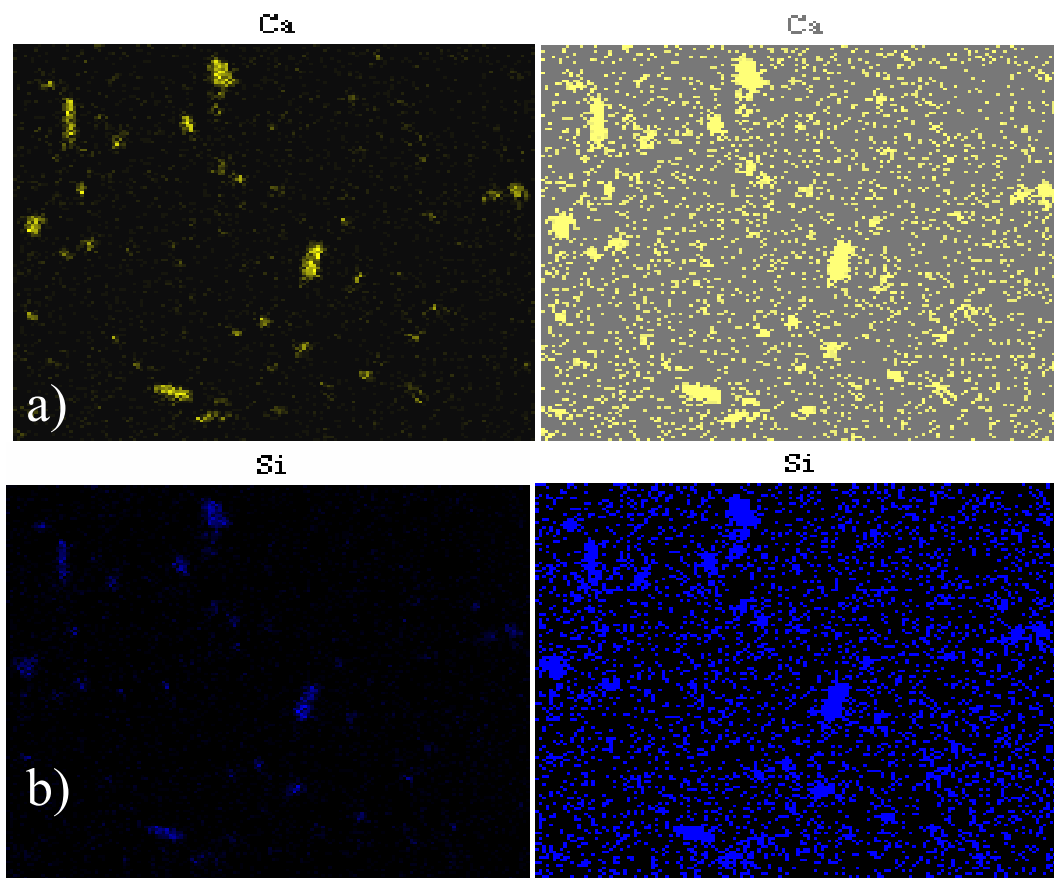


Figure 10. Elemental mapping of a) Calcium and b) Silicon with corresponding images with improved brightness and contrast

Another measure of dispersion is the change in clarity of the material with the addition of fillers. Light scattering is dependent on the size and distribution of the particles in the resin matrix and frequently it has been observed that smaller particles scatter light more than larger particles in polymer composites [8]. However, when the particles are small, usually smaller than the wavelength of light, scattering reaches a peak and light scattering begins to decrease with decreased particle size. This is attributed to the transfer of scattering dominance to Rayleigh scattering from Mie scattering [9]. This peak in light scattering is dependent on other factors such as refractive index and shape but for spherical particles the peak has been estimated to be between 100 and 250 nm [9] and can be as high as 3 μm [8].

Figure 11 illustrates the effect of the nanomaterials on the optical clarity of CYCOM® 977-3. Sample 11b, 3% R202, had a significant impact on the transparency of the neat 977-3 epoxy system. The letters behind the sample can only be faintly read through the sample. This is supported by the TEM images showing a large number of aggregates in the 100-200 nm range. The 5% 520H, sample 11c, had approximately the same transparency as the neat resin and only lightened the color. This confirms what was seen in the TEM and SEM images about the dispersion and size of the aggregates. Very few particles were seen in the 100-250 nm range indicating that the majority of the particles are much larger and much smaller. The optical

clarity of the $\text{Ph}_{12}\text{T}_{12}$ material, sample 11d, was more opaque than the wollastonite but clearer than the R202 sample. This implies that the dispersion and size distribution of aggregated particles of the $\text{Ph}_{12}\text{T}_{12}$ is less than that of the 520H in the epoxy.

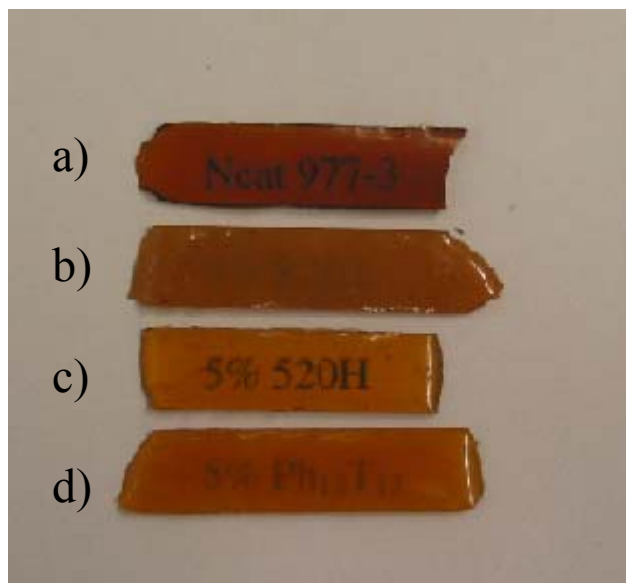


Figure 11. Comparison of optical clarity. Sample a) is neat 977-3 epoxy resin, b) is 3% R202 modified 977-3, c) is 5% 520H modified 977-3 and d) is 5% $\text{Ph}_{12}\text{T}_{12}$ modified resin

3.2 Parallel Plate Rheology From a processing standpoint it is important to make sure that the addition of nanoparticles does not adversely affect the viscosity of the epoxy resin system. In order to quantify the affect of nanoparticles on the viscosity of the material, parallel plate rheology was performed. The test executed was a steady state rotational test at various shear rates and the samples investigated included 977-3 epoxy with 5 wt% of the three different nanofillers. The samples were prepared by mixing component C into the mixtures of components A and B with the mini high shear mixer, T25, for the five minute duration and samples were run without the addition of component D. The tests were performed at two different temperatures, room temperature and 80°C.

The room temperature data in Figure 12 show that the R202 is shear thinning with an initial viscosity of 44,400 Pa·s and a final viscosity 56 Pa·s. This is almost 3 orders of magnitude greater than the unmodified resin at the low shear rates and approaches the viscosity of the neat resin at high shear rates. The viscosities of the neat resin and mixtures of 520H wollastonite and $\text{Ph}_{12}\text{T}_{12}$ are Newtonian up to a shear rate of 1 s^{-1} with viscosities of 73, 83, and 101 Pa·s respectively. Above this shear rate, all three materials exhibit a slightly shear thinning behavior with reduction in viscosities of less than 20 Pa·s. This is important because many resin processing techniques require low viscosity. For example, resin transfer molding (RTM) is a low pressure process and typically uses resins with viscosity less than 0.8 Pa·s. Resin film infusion (RFI) is capable of handling higher viscosity materials but still uses temperature to reduce viscosity for processing. Lower viscosity materials are preferable because higher temperatures decrease the working time during processing [10].

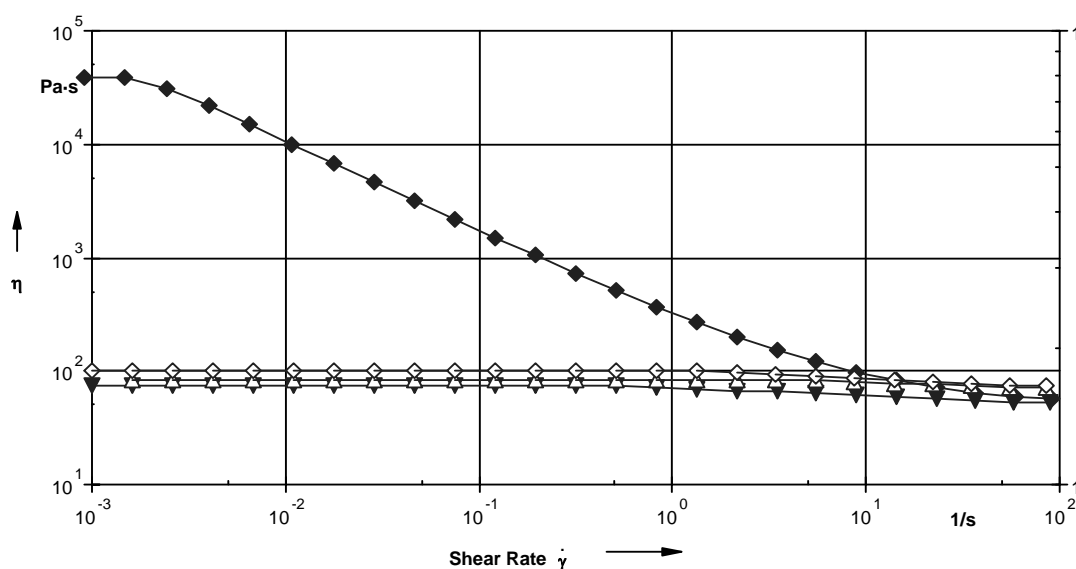


Figure 12. Viscosity of nanomaterials with respect to shear rate. \blacklozenge is 5% R202, \blacktriangledown is neat 977-3, Δ is 5% 520H, and \diamond is 5% Ph₁₂T₁₂.

The elevated temperature, 80 °C, data are shown in Figure 13. The trends in the viscosity for the elevated temperature data are similar to those seen in the room temperature data in Figure 12. The neat epoxy and the 520H mixture are Newtonian and have no statistical difference in viscosity from each other. The Ph₁₂T₁₂ displays a small amount of shear thinning and the R202 sample has a non-Newtonian viscosity ranging from 3.5 to 0.5 orders of magnitude greater than the neat epoxy.

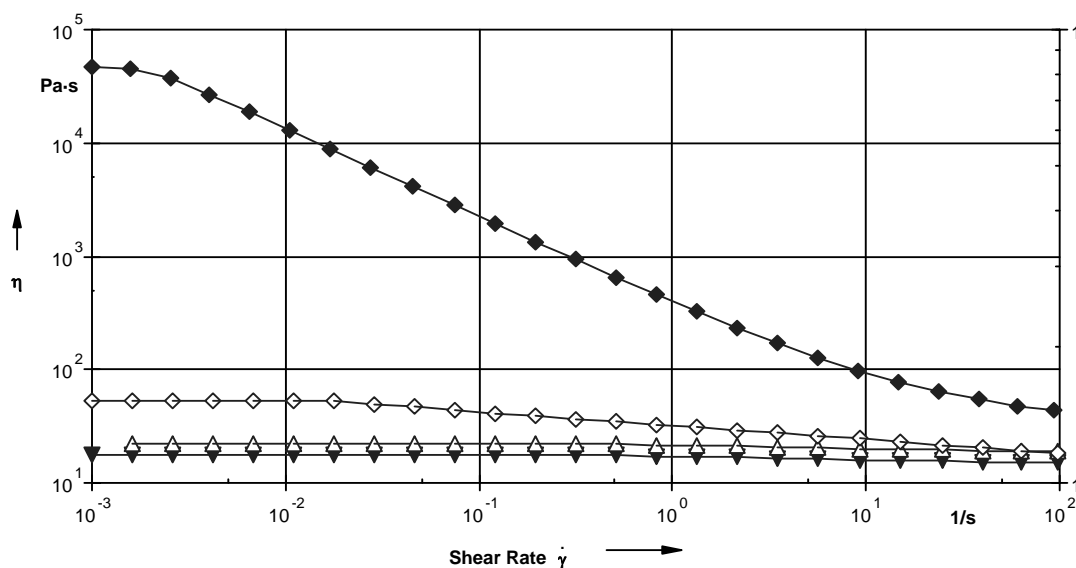


Figure 13. Viscosity of nanomaterials with respect to shear rate. \blacklozenge is 5% R202, \blacktriangledown is neat 977-3, Δ is 5% 520H, and \diamond is 5% Ph₁₂T₁₂.

3.3 Thermal Analysis The industrial process for formation of this material involves mixing all the components in a single batch using a paddle mixer. To mimic this technique on a lab scale for our control, the neat material was mixed using a stir bar and heated in an oil bath. DMTA tests were performed on the cured material and the glass transition temperature was determined by the peak in the loss modulus (E'') curve and the peak in the tan delta curve. The resulting T_g data is shown in Table 1. In order to confirm the process, the T_g of the neat resin material was compared to the data provided by CEM. The data show a slight difference, less than 10%, for the $E'' T_g$ and no difference between the T_g by the tan delta.

Table 1. DMTA results for nanomaterials

| Sample # | Description | $E'' T_g$ (°C) | $\tan \delta T_g$ (°C) |
|----------|---|----------------|------------------------|
| 1 | Neat 977-3 – stir bar | 217 | 248 |
| 2 | Neat 977-3 – CEM provided data | 196 | 248 |
| 3 | 3% R202 – stir bar – acetone | 172, 260 | 198, 287 |
| 4 | 3% R202 – stir bar – methylene chloride | 148, 275 | 180, 247 |
| 5 | 3% R202 – high shear – 5 min | 135 | 167 |
| 6 | 3% R202 – high shear – 5 min – dried | 145 | 176 |
| 7 | 3% R202 – high shear – 30 min | 177 | 211 |
| 8 | 3% R202 – high shear – 30 min – 70 °C | 202 | 251 |
| 9 | 5% 520H – high shear – 5 min | 135 | 169 |
| 10 | 5% 520H – high shear – 5 min – dried | 151 | 177 |
| 11 | 5% 520H – high shear – 30 min | 187 | 234 |
| 12 | 5% 520H – high shear – 30 min – 70 °C | 206 | 252 |
| 13 | 5% Ph ₁₂ T ₁₂ – high shear – 30 min – 70 °C | 202 | 251 |

3.3.1 R202 – Aerosil Nanosilica When R202 was added to the material, the viscosity increased noticeably. This made using a stir bar very difficult because of the weak nature of the stirring mechanism. After consulting with CEM, the authors investigated the effect of adding a solvent, acetone, which proved unsuccessful. Further conversations with CEM revealed that methylene chloride may be an alternate solvent due to lower boiling point. Both solutions, samples 3 and 4, showed two peaks in the loss modulus, E'' , and tan delta response. Figure 14 is included to illustrate this result. This phenomenon is not fully understood but the authors hypothesize that this indicates a two phase immiscible system and concluded that the mixing was inadequate.

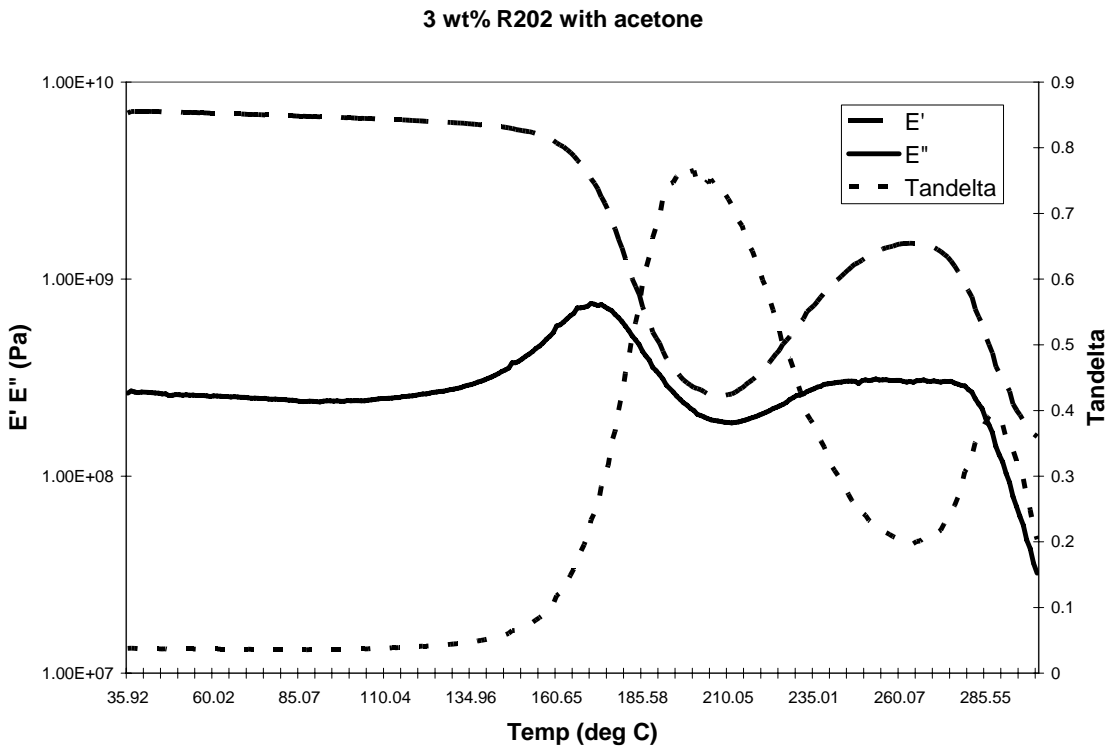


Figure 14. DMTA curves for 3 wt% R202 mixed with acetone

In order to get away from the use of solvents and improve mixing, a mixing technique using a mini high shear mixer, IKA T25, was employed to incorporate component C into the material. The use of a rotor stator mixer to mix in the components was highly efficient and could be accomplished very quickly, 5 minutes. However, the reduction in mixing time appears to hinder the proper formation of the epoxy structure required to maintain the mechanical integrity of the material. This is evident in the T_g results of samples 5 and 6. The procedure was then altered to mix the component C with the modified A and B mixture for thirty minutes. After thirty minutes of mixing, the T_g of sample 7 improved significantly in comparison to sample 5. However, the T_g results were still not in the range that was expected based on information from CEM and results by Koo et al. [2].

The mixing procedure used by Koo and colleagues calls for component C to be mixed into components A and B at an elevated temperature [11]. The authors investigated the possibility of generating the required heating via the high shear, high friction process. To test this concept the temperature readings from the outside of the beaker were continuously taken using a thermocouple attached to the beaker and temperature readings of the actual material were taken periodically during the thirty minutes of mixing. When the temperature of the actual material was taken, the mixer was turned off and a thermocouple was inserted into the material. Figure 15 shows that the heat incorporated by the shear was under 50 °C, less than the optimum mixing temperature of 70 °C.

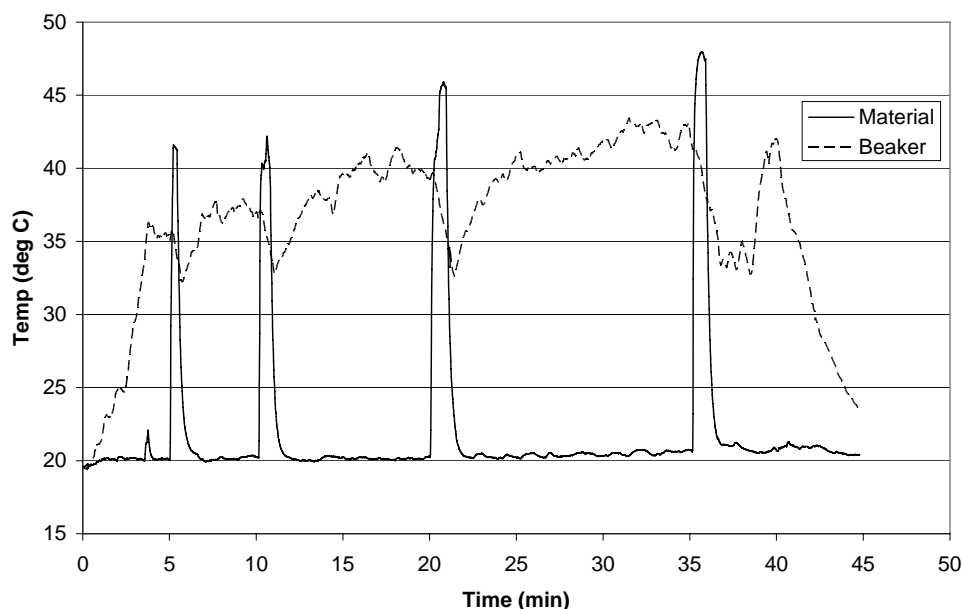


Figure 15. Mixing temperature of 520H with measurements continuously from the outside of the beaker and intermittently from the material.

The mixing procedure was then modified to include external heating of the material using an oil bath. After roughly 25 minutes of mixing, the material noticeably thickened. The samples were cured and the T_g achieved for sample 8 was in the expected range based on past work by Koo et al. [2].

Furthermore, one will recall that samples for parallel plate rheology were mixed for five minutes and tested at 80 °C. That data shown in figure 13 show there is no increase with time when subjected to low shear deformation for approximately one hour. This indicates that the interaction of the material requires mixing as well as time and temperature. To further investigate this phenomenon, samples were tested in a differential scanning calorimeter (DSC). The materials were tested using an isothermal hold at 80 °C for three hours. No reaction was observed for the material in that time and temperature, further supporting the conclusion above.

3.3.2 520H Wollastonite The next nanoparticle investigated was a modified calcium silicate wollastonite 520H. The same high shear mixing techniques were applied to the 520H samples as with the R202. In Table 1 samples 9 through 12 use the same mixing procedures as samples 5 through 8, modified with R202. The same pattern in T_g with respect to mixing technique can be seen in both materials and in fact, the T_g of both materials are very similar. This repeated pattern further demonstrates that mixing time and temperature are critical to the formation of the epoxy structure.

3.3.3 $Ph_{12}T_{12}$ POSS The third nanoparticle explored was a polyhedral oligomeric silsesquioxane DodecaPhenyl-POSS ($Ph_{12}T_{12}$). A 5% POSS composite, sample 13, was made using the

optimized mixing technique. DMTA of sample 13 showed that the T_g of the material was approximately the same as the R202 and 520H.

4. CONCLUSIONS

The CYCOM® 977-3 was modified by three types of nanofillers, R202 nanosilica, 520H wollastonite and $\text{Ph}_{12}\text{T}_{12}$ POSS. The mixing technique of the nanocomposites proved critical to the resulting thermal properties. Although the high shear mixer was able to mix components in less time than the stir bar technique, time and temperature were necessary for the evolution of the epoxy structure needed for optimal properties.

With the final mixing technique, using the mini high shear mixer for 30 minutes at 70 °C, all three nanomaterials show little improvement in T_g over the neat epoxy. Because the 520H and the $\text{Ph}_{12}\text{T}_{12}$ do not affect the Newtonian viscosity of the material, these materials should be explored in more detail to discover if an optimum loading can be found to improve the thermal properties of the materials. Future work should also encompass other types of POSS to determine if additional improvements can be made.

5. ACKNOWLEDGEMENTS

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